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NANOSCALED MAGNETIC ELECTRODEPOSITED STRUCTURES ON THE BASIS OF ION GROUP METALS: PREPARATION, STRUCTURE, MAGNETIC AND MAGNETORESISTIVE PROPERTIES

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1. Introduction

At the present time the emphasis of the investigations in almost all the branches of science, including magnetism, is shifted towards the study of 'nanoscaled', or so called 'nanosized' objects. The interest in such materials derives from the unusual, often unique properties associated with the relatively high ratio of the numbers of surface and bulk atoms. The classification of nanoscaled objects is not clearly defined, but a general definition may be given as follows: nanoscaled materials are those in which any parameter, e.g. the grain size, layer thickness, the size of columnar crystal, diameter of magnetic inclusion, etc., is of the same order as the fundamental constants of the substance - such as free electron path, Fermi wave vector, etc.

Magnetic nanosized materials that are based on transition metals may be divided into six main groups (Fig.1). They are: films with columnar type of crystal structure (1), multilayers (2), granular or so called inhomogeneous alloyed films (3), quasi- or semigranular films (4), nanocrystalline films (5) (which are produced after partial crystallization of amorphous soft magnetic films and foils) and, finally, nanowires (6). There is no sharp boundary (transition) between these types of nanosized materials: for example, it is possible to produce multilayered nanowires and columnar type films. Multilayers with very thin alternate magnetic and nonmagnetic layers look like, and behave like, granular films. Therefore, the investigation of each separate nanosized magnetic material, and also of the permanent transitions from one type to another, can give us additional information about each individual material, and also about the common properties of the class of materials.

It is necessary to say that all of the above mentioned classes of nanoscaled materials can be produced in a variety of forms by the electrodeposition method, and some of them (e.g. nanowires) may be prepared exclusively by electrochemical means.

The advantages of electrodeposition, such as low cost, potentially high productivity, and the ease of automation of the process make electrodeposition a very attractive technique with possible commercial viability. Preparation of nanoscaled materials by electrodeposition technique becomes increasingly widespread all over the world, for example, in UK, France, Switzerland, Japan, USA, Holland, Germany, etc.

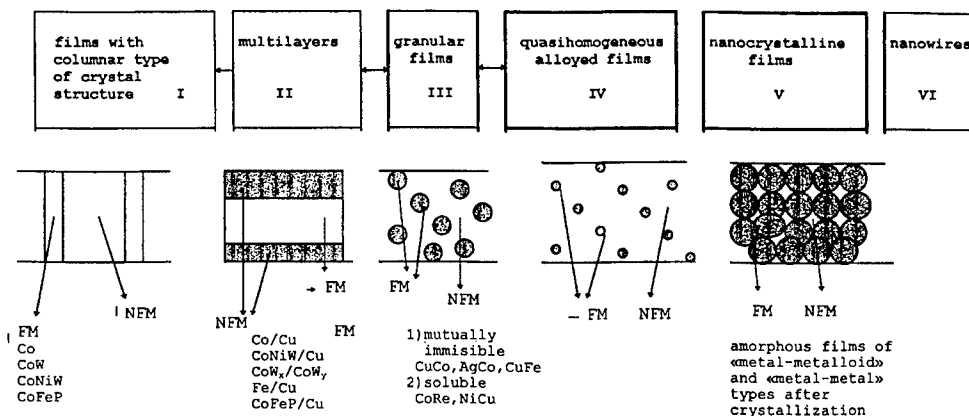


Fig.1. The scheme of nanosized electrodeposited materials.

2. Films with columnar type of crystal structure

One of the ways to increase the magnetic recording density in storage devices is to use a new, vertical mode of recording. The data-storage capacity of a device using such a mode could be increased by more than an order of magnitude over similar systems that use the traditional horizontal recording mode. It is necessary to use recording media with the unusual magnetic property of high perpendicular anisotropy for such applications, so as to allow a stable remanent magnetization component to be achieved perpendicular to the plane of the film. The crystalline anisotropy of ferromagnetic metals, (i.e. [002] texture of hcp-Co structure), alone would be insufficient to provide the required magnetic properties; since the demagnetization energy $E_{dm} \sim 2\pi M_s^2 \sim 10^7 \text{ erg/cc}$ would be still higher than the crystallographic energy $E_A \sim 4.2 \times 10^6 \text{ erg/cc}$. It is possible to overcome the demagnetization energy, which tends to arrange the magnetization vector into the plane of the films, by decreasing the magnetization of the material (but this not the best way), or by adding to crystallographic energy some other contribution. This could be, for example, the shape anisotropy energy of columnar grains in recording media. Films exist in which nanosized ($\sim 10 \text{ nm}$) 'needle-like' crystallites - columns, which pass through the full thickness of the film, are surrounded by regions with lower, or even zero, magnetization, (Fig.2). In such a case the sum of

crystallographic energy plus the shape anisotropy energy of columnar grains can overcome the demagnetization energy.

Films with columnar type of crystal structure can be produced also by electrodeposition method [7]. There are two requirements for this. The rate of appearance of new grains must be much smaller than the rate of growth of existing crystallites; and the velocity of growth of grains perpendicular to the plane of the film must be much higher than the in-plane growth rate. This may be achieved by choosing electrodeposition regimes where passivation of the growth surface is very extensive due to the formation of hydroxides.

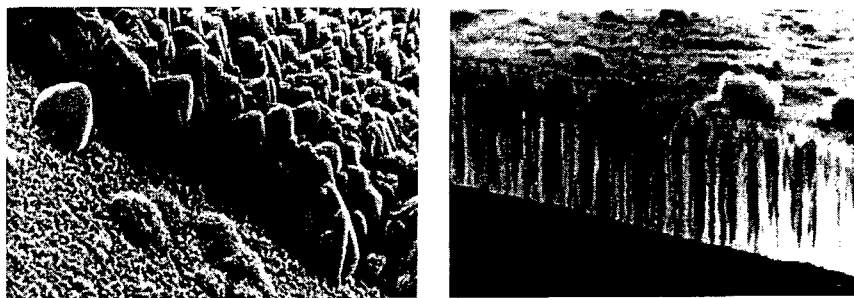


Fig.2. Films with different types of crystal structure. Magnification - 50000^x

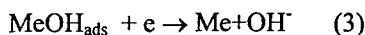
A possible interpretation of the mechanism of columnar structure growth for electrodeposited film (such as Co/Ni) is as follows. In electrolytes with high pH, the formation of metal-hydroxide complexes (in our case of Co and Ni) of the form MeOH^+ and $\text{Me}_4\text{OH}^{4+}$ is highly probable. These positively charged complexes are formed by reactions of the type shown below,



(where Me are Co and Ni). These complexes migrate towards the cathode, where they capture an electron and are adsorbed onto the cathode surface,



The adsorbed complexes are then further reduced by the reaction



Thus, besides the reduction of hydrogen, alkalization also occurs at the cathode. It should also be noted that the diffusion coefficient of complexes of type (1) is some

orders of magnitude higher than that of simple metal ions; therefore reduction of metal atoms (Co, Ni, Fe) is most likely to take place not from metal ions but from their complexes with hydroxide groups. It has been established experimentally that the number of the adsorbing complexes of $\text{Me}(\text{OH})^+$ and $\text{Me}_4(\text{OH})_4^{4+}$ on the most closely packed (001) face is about 1.8 times higher than on the others. Therefore, the recovery of Co and Ni ions, occurring through the formation and subsequent fission of their hydroxide complexes, will result in a more rapid growth of closely packed planes. Thus, the pH value of the electrolyte being relatively high and the quantity of the adsorbing $\text{Me}(\text{OH})^+$ and $\text{Me}_4(\text{OH})_4^{4+}$ complexes formed being large, is therefore expected to result in the development of the [001] texture, (the closely packed planes will be parallel to the cathode surface). Addition of alkaline at the cathode due to reaction (3) causes an increase in pH by 3-4, i.e. with a pH of the electrolyte in the volume equal to $\sim 6.0 - 7.0$ pH, it increases, locally, at the cathode, to between 9 and 10. It has been well documented, that the reaction of the type:



accelerates rapidly at $\text{pH} = 7$.

It is therefore necessary to ensure that the rate of reaction (4) in the electrolytes used is very high, so as to achieve the required texture. The hydroxides of cobalt and nickel, forming in great quantities, migrate from the areas of active crystal growth (i.e. from the grain center with [001] texture) to the crystallite periphery, where the growth rate is lower (the faces with orientations of (100) and (101) grow approximately 1.8 times slower). Accumulating in large quantities, they are trapped during the growth and thereby form rather broad inter-grain regions. The resulting structure is of columns of [001] cobalt surrounded by regions which are highly enriched in nonmagnetic hydroxide $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$. Under optimum deposition conditions, this mechanism of structural growth is sufficiently stable. When the electrolysis conditions deviate from the optimum, two possible modes of growth are observed. Normal growth of crystallites occurs when the crystallite growth is very much greater than the rate of formation of new crystallites ($D \leq 3 \text{ mA/cm}^2$) and deposits obtained are large-grained, not textured, since the growth rate of different faces is about the same. Dendrite growth occurs for $D \geq 100 \text{ mA/cm}^2$, where the rate of growth is very much less than the rate of formation of new crystallites; the resulting structure is fine-grained, not textured. The columnar crystallite growth (Fig.2) is intermediate between the normal and dendrite types of growth. The increase in the ratio of crystallite growth over that of crystallite formation is characteristic of it. It is essential, however, to note that under conditions of columnar growth the growth rate for different faces varies widely. When the electrochemical conditions of formation are in marked contrast to those that are optimum for the columnar growth of the films, i.e. when the quantity of the adsorbing $\text{Me}(\text{OH})^+$ and $\text{Me}_4(\text{OH})_4^{4+}$ complexes is small, the experimentally observed development of structure

and texture of deposits can be accounted for in terms of the models of normal and tangential crystallite growth [8].

Depending on the conditions of preparation, (both composition and regimes of electrodeposition - pH, D_k and T), it is possible to regulate not only the type of crystal structure but also to determine, over a wide range, the diameter of grain columns and the intercolumnar distance. As a result, the magnetic properties of films, including the perpendicular or in-plane anisotropy, could be varied over a wide spectrum. We were able to measure magnetic parameters such as the remanent magnetization perpendicular to film plane direction $M_{r\perp} = 0.1 - 0.3$ ($M_{r\perp} > M_{r\parallel}$, by 2 - 3 times) and coercive force in the same direction $H_{C\perp} = 1000 - 2000$ Oe ($H_{C\perp} > H_{C\parallel}$) [9]. The indicated parameters of electrodeposited Co-Ni hard magnetic films with perpendicular anisotropy and a columnar type of crystal structure suggest their applicability to vertical-mode storage devices.

3. Multilayered films

Relatively recently, extensive work on the development of methods for deposition and study of physical properties of multilayered magnetic structures with ultrafine (<1 nm) alternating magnetic and non-magnetic layers has been carried out. These structures are remarkable, not only from a fundamental viewpoint, but also because they have a wide practical application due to their unique magnetic, mechanical, electronic and other properties.

The initial approach to achieving high perpendicular anisotropy in multilayers was influenced by experience with the hard magnetic films with the columnar structure described above [10]. This approach relies upon the so-called surface anisotropy. In very thin magnetic films, (of the order of a few nanometers), regardless of whether they are single-layered or multilayered, the component of the magnetization vector that is perpendicular to the plane of the film increases as an inverse function of film thickness. In multilayered thin film structures, consisting of alternate magnetic and nonmagnetic layers, every magnetic layer has two surface sublayers (at each interface boundary). If the thickness of magnetic layers is such that the material at the boundary between layers is a significant proportion of the bulk volume of the layer, high anisotropy can be achieved after the growth of many such alternate layers.

One feasible, and technologically simple, method of producing multilayered structures is electrodeposition in a pulse regime. A multilayer can be obtained in this way from a single electrolyte. Ferromagnetic metals such as Co, Fe and Ni or their alloys, and copper or (Ag, Au, Pd) can be used for magnetic and nonmagnetic layers, respectively. Electrochemical deposition of such structures relies upon the fact that the equilibrium reduction potentials of the ferromagnetic and non-ferromagnetic ions differ by more than 400 eV. In general, electrolytes that are saturated in copper are used in the multilayer deposition process. This is due to transport difficulties in the electrolyte, which limit the current density for copper deposition when the solution is dilute in



Fig.3. Multilayered Co/Cu film.
The thickness of layers in 5 nm.

copper ions. The concentration of the ferromagnetic ions (in this case Co) must be very much less than that of the Cu ions. In this case, if a current density of 0.53 mA cm^{-2} is used during the Cu deposition pulse, this will be much less than the minimum current density of cobalt deposition, which is about 5 mA cm^{-2} . This, therefore, results in a pure Cu layer. For deposition potentials as low as circa 0.87 V , only copper will deposit and above this both copper and cobalt deposit. The current density used during the deposition of the magnetic layer was 100 mA cm^{-2} , hence the deposition rate of the ferrometal exceeded by about two orders of magnitude that of copper. The

proportion of copper in cobalt layers could not therefore exceed a fraction of a percent. In such a manner, using a single solution and pulse regime of electrodeposition we are able to obtain the desired Co/Cu multilayered structure (Fig.3), where the layer thickness was determined by pulse duration.

The X-ray diffraction patterns of the Co/Cu multilayered films reveal two features: the absence of any reflection in a small-angle range and satellite reflections near the basic structure reflections of Co. When the thickness of the Co layers was changed, with a constant Cu layer thickness ($d_{\text{Cu}}=1.5 \text{ nm}$), the X-ray diagram was as follows. The first reflections appeared at $T \approx 80 \text{ nm}$ ($d_{\text{Co}}=1.5 \text{ nm}$), with a corresponding cobalt deposition pulse time of $T_{\text{Co}} \approx 200 \text{ ms}$ ($d_{\text{Co}}=2.5 \text{ nm}$); there were three obvious reflections of different intensities. The reflections at $2\theta = 49.5^\circ$ and 53.8° are the satellite reflections of the structure peak at $2\theta = 52.1^\circ$ for (111) fcc Co (tabulated $2\theta = 51.95^\circ$). With further increases in T_{Co} (up to 400 ms), the picture becomes more distinct. Apart from the satellite reflections of the peak for (111) fcc Co, one more reflection appears for (200) fcc Co ($2\theta = 60.7^\circ$) with satellite reflections ($2\theta^- = 58.5^\circ$, $2\theta^+ = 62.5^\circ$). In all the investigated Co and Cu layer thickness ranges, (up to 10 nm), the multilayer Co/Cu structures, (obtained by electrodeposition from a single solution), were structures based on fcc Co and fcc Cu. In addition, the conjugation of Co and Cu layer structures took place on more compact planes ((111) fcc Co || (111) fcc Cu).

The presence of a satellite reflection is confirmed by the fact that the modulation period of the inter-plane distances of the Co/Cu, calculated from the satellites for different reflections, are consistent with the compositional modulation obtained using Auger spectroscopy.

According to the Auger profile some amount of one element may be present in the layers of the other element (5 - 15%), but this experimental result may be explained in another way. When the thicknesses of the alternate layers are very small, irregularities on the sub-micron scale result in protrusions of material from one layer to the next. The diameter of the Auger spectroscopy probe was $1 \mu\text{m}$ and some of these protrusions are,

therefore, necessarily sampled by the Auger process. The irregularities of the thin layers in periodic structure can be estimated to be up to $\sim 15\%$.

From an analysis of these figures and the magnetic behavior reported below, it is shown that the ultrathin alternating Co/Cu multilayers are 'island'-type layers. When the layer thickness is less than 1 nm, the irregularity of the layers is of the order of $\sim 50\%$. Structural investigations using transmission electron microscopy confirmed the island-like type structure of the layers. At Co deposition pulse times of less than 200 ms, the Co layer forms islands of 15 - 30 nm in diameter. Microdiffraction studies show the presence of crystallites of fcc Co.

The value of the total magnetic anisotropy constant of an ultrathin magnetic layer in Co/Cu multisystems can be given as the sum of the crystallographic strain, and surface anisotropy components. The contribution of the surface anisotropy constant to the perpendicular magnetic anisotropy becomes predominant when the magnetic layer thickness in the multilayers is of the order of a few nm. As the thickness of the Co layer decreases, the perpendicular anisotropy and coercive force increase (Fig.4). Additional evidence of the development of perpendicular magnetic anisotropy can be seen from the magnetization reversal curves parallel and perpendicular to the coating directions.

As the thickness of the magnetic layers of Co decreases, the remanent magnetization M_r and H_c in the direction perpendicular to the surface of films increases. Simultaneously, the equivalent in-plane parameters decrease. This is typical of magnetic structures with increasing perpendicular anisotropy. Analyses of these figures show that the decrease in the Co layer thickness leads to an increase in the perpendicular magnetic

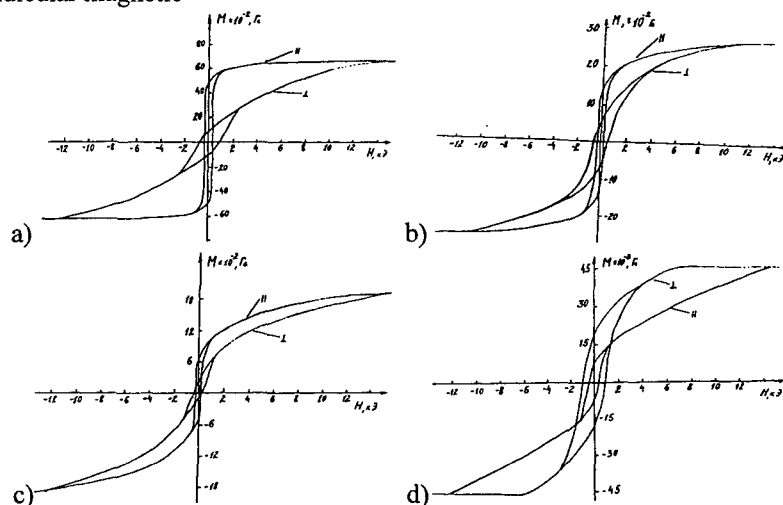


Fig.4 Magnetization curves of Co/Cu multilayers with time of pulse Co deposition: a - $t_{Co} = 10$ ms, b - 40, c - 15 and d - 10 ms; $t_{Cu} = 5$ s = const.

anisotropy constant. Furthermore, in our opinion, the increase in the discontinuity of these layers is the reason for the increase in coercivity of the island-type structure. This fact is an important result for the use of the investigated multilayer films as materials for vertical magnetic recording.

We reported on studies of multilayered films of the Co/Cu, Fe/Cu, CoFeP/Cu and CoNiW/Cu systems. An anomalous temperature dependence of the magnetization of the Co/Cu films was found [12]. One of the possible explanations was based on the existence of indirect exchange (RKKY) coupling observed at thickness of Co and Cu layers that led to the antiferromagnetic ordering of magnetization vectors of adjacent layers. This coupling is also responsible for GMR in multilayered films. Therefore, we continued our experiments with the investigation of the magnetoresistance of multilayered Co/Cu films [13]. To study the magnetoresistance, we used films deposited on a pyroceram substrate with a chemically deposited layer of amorphous nickel phosphide as well as on an aluminum foil substrate that was later dissolved in a 10% NaOH solution. The measurements showed virtually identical results for the films deposited on nickel phosphide and on aluminum because of the low shunting effect of the nickel phosphide layer. Thus, the films deposited on the pyroceram substrate were of better practical use in our experiments. The magnetoresistance was measured in a temperature range of 300 – 10 K in fields of up to 1.3 T, (in steps of 0.005 T), by the four-point method. We used three configurations, differing in the orientations of the current I , field H , and the film plane. They were designated $\Delta R_{||}$ (where both current and field were parallel to the film plane), ΔR_{\perp} (where the current was perpendicular to the in-plane field); and $\Delta R_{\perp||}$ (where the field was perpendicular to the in-plane current).

It is known that, in contrast to the anisotropic magnetoresistance of ferromagnetic metals and alloys, the giant magnetoresistance of multilayered films is not only characterized by a large value (more than 60%), but is also isotropic for measurements using any combination of relative directions of the applied magnetic field, current, and film plane (i.e., $\Delta R_{||}$, ΔR_{\perp} and $\Delta R_{\perp||}$).

Figure 5 shows $\Delta R_{||}$ as a function of the thickness of the cobalt and copper layers. Negative magnetoresistance (its decrease upon magnetic saturation) which is a prerequisite of the GMR, was observed for the films consisting of cobalt and copper layer thickness of 14.0 and 15.0 nm (Fig.5(a,c)) and 0.2 and 1.5 nm (Fig.5(b)) respectively. The $\Delta R_{||}(H)$ dependence (Fig.5(a)) shows a positive magnetoresistance typical of the conventional anisotropic magnetoresistance of a film consisting of the cobalt and copper layers of the thickness indicated. The $\Delta R_{||}(H)$ dependence (Fig.5(b)) characterized by a broad "triangular" reversible maximum without saturation and hysteresis, (observed at both 300 and 100 K), may be typical of the following two cases. First, the absence of hysteresis may be explained by a strong antiferromagnetic coupling of magnetic layers. In the studies of the structure of periodic Co/Cu multilayered films described above, it was shown that ultrathin cobalt layers (less than 1 nm in thickness) consisted of isolated "islands" of Co, whose diameter was an order of magnitude greater than the film thickness. These magnetic "islands" of Co in the copper

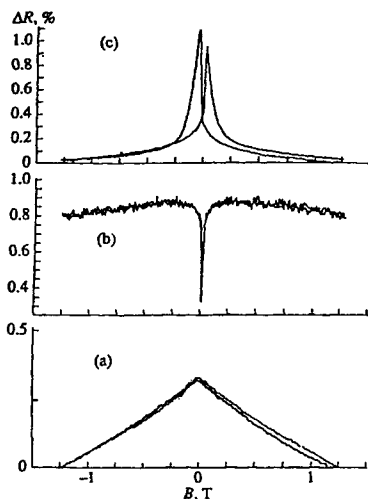


Fig.5. Field dependence of magnetoresistance taken at room temperature in field parallel to the in-plane current for the Co/Cu multilayered films with various thickness of the layers:

- (a) $d_{\text{Co}} = 0,2 \text{ nm}$ and $d_{\text{Cu}} = 1,5 \text{ nm}$;
- (b) $d_{\text{Co}} = 2,5 \text{ nm}$ and $d_{\text{Cu}} = 1,5 \text{ nm}$;
- (c) $d_{\text{Co}} = 14 \text{ nm}$ and $d_{\text{Cu}} = 15 \text{ nm}$.

matrix may be ordered antiferromagnetically because of the magnetostatic coupling through their stray fields. Without an applied magnetic field, the magnetic single-domain particles will have antiparallel mutual orientations because the energy of the system on the whole tends to a minimum. The electrical resistivity of such a film in the initial state is higher than after its magnetization to saturation. The electron scattering on such magnetic inhomogeneities is isotropic ($\Delta R_{\parallel} \approx \Delta R_{\perp}$) and thus represents a possible mechanism for the giant magnetoresistance in the Co/Cu films with cobalt and copper layers of 0.2 and 1.5 nm in thickness, respectively. Secondly, such a field dependence $\Delta R_{\parallel}(H)$ is also typical of granular (heterogeneous) alloys that display giant magnetoresistance. In these alloys, the effect of GMR is attributed to a superparamagnetic state of magnetic granules surrounded by a nonmagnetic matrix. The increase in the giant magnetoresistance and weak hysteresis observed at a temperature of 10 K in our samples are typical of granular alloys. Thus, the Co/Cu film consisting of the cobalt and copper layers of 0.2 and 1.5 nm in thickness, respectively, may be considered to be a granular multilayered material.

Figure 5(b) shows the field dependence $\Delta R_{\parallel}(H)$ for the Co/Cu films with $d_{\text{Co}} = 2.5 \text{ nm}$ and $d_{\text{Cu}} = 1.5 \text{ nm}$. As is seen, the increase in the thickness of the magnetic layer resulted in the transition from isotropic (negative ΔR_{\parallel} and ΔR_{\perp}) to anisotropic (positive ΔR_{\parallel}) magnetoresistance typical of homogeneous magnetic materials. The disturbance of the mechanism causing GMR is likely to be due to the imperfect structure of the copper interlayer and the formation of ferromagnetic Co "bridges" between the layers. These "bridges" connect the layers in a uniform interacting medium, yielding the usual anisotropic magnetoresistance typical of ferromagnetic materials. To obtain information on the quality of the structure of this $\text{Co}_{2.5 \text{ nm}}/\text{Cu}_{1.5 \text{ nm}}$ multilayered system, we studied the films by nuclear magnetic resonance, using ^{59}Co as a source (Fig.6).

The maximum observed at 21.6 T is close to that observed in bulk fcc Co ($B_{hf} = 21.6$ T). However, the peak is very broad and extends over the range of hyperfine fields from 18.4 to 22.6 T; the extreme points of this range correspond to bulk hcp Co (22.6 T) and to Co atoms having 1 or 2 nearest-neighbor nonmagnetic atoms of Cu ($B = 18.4$ T). Because of the enhanced imperfection of the structure and the presence of a large concentration of Co atoms that have one or two Cu atoms in their nearest neighborhood, as well as the possible existence of ferromagnetic «bridges» between the cobalt layers, such a system exhibits the conventional anisotropic magnetoresistance. The experimental data confirm that, on increasing thickness of the nonmagnetic layer to 2.5 nm (at $d_{Co} = 2.5$ nm), the structure becomes more perfect and ferromagnetic “bridges” between the magnetic layers disappear, and the negative giant magnetoresistance appears instead of the positive anisotropic magnetoresistance (Fig. 5(b)). Interesting data were obtained for multilayered films consisting of relatively “thick” (~ 10.0 nm) layers. These results show that the antiferromagnetic coupling is by no means necessary for giant magnetoresistance to arise. The magnetoresistance curve differs from the bell-shaped curves typical of the films with strong antiferromagnetic coupling between the magnetic layers; it has two maxima located at fields $\pm H_C$ (H_C is the coercive force or the switching field at which the magnetization passes through zero). Thus, the maximum values of the magnetoresistance correspond to the state at which the domains of the adjacent magnetic layers are oriented randomly. An abrupt change in magnetization leads to an abrupt decrease in electrical resistivity. The magnetoresistive sensitivity, i.e. the change in the magnetoresistance per unit magnetic field, is an important parameter of magnetoresistive materials used in magnetic-field sensors. It was important that, in contrast to these films, the decrease in the electrical resistivity in the films studied in this work occurs at low fields ($H < 0.01$ T). The highest magnetoresistive sensitivity was equal to 1.5% at magnetic field changes of $\pm T$; the saturation field was 0.025 T.

In summary, we observed the giant magnetoresistance in Co/Cu multilayered

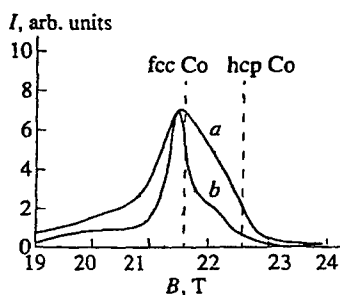


Fig. 6. NMR spectra for the Co/Cu multilayered films with $d_{Co} = 0.2$ nm and $d_{Cu} = 1.5$ nm (a) and $d_{Co} = 10$ nm and $d_{Cu} = 7$ nm (b).

films produced by pulsed electrodeposition from a single electrolyte. For the first time, we found the low-field giant magnetoresistance. This is of great practical interest. It is obvious that electrodeposition shows promise as a production method of giant magnetoresistive films. It is interesting to produce and study magnetic multilayered films with magnetic layers having a low coercivity. Electrodeposited CoFeP/Cu multilayered films, exhibiting a low coercive force and high thermal stability, are expected to be promising materials with a low-field giant magnetoresistance higher than that of the Co/Cu films. Moreover, electrodeposition may be used to

produce even more promising multilayered films exhibiting "spin-valve" magnetoresistance effects [14]. These films consist of five or more alternating layers, for example, magnetically soft/nonmagnetic/ magnetically soft/magnetically hard/nonmagnetic layers. The "spin-valve" magnetoresistance may be observed in such films as $(\text{CoFeP}_x/\text{Cu}/\text{CoFeP}_x/\text{CoFeP}_y/\text{Cu})_n$ and $\text{CoW}_x/\text{Cu}/\text{CoW}_x/\text{CoW}_y/\text{Cu})_n$, where the magnetic alloys with $x > 20$ at.% have low coercive force and those with $y < 5$ at.% have high coercivity. The composition and magnetic properties of the alternate layers may be varied by controlling the amplitude of applied current pulses. The investigations of the above mentioned films are now in progress and the results will be reported in further papers.

4. Granular films.

As we showed in section 3 of the present paper, multilayered films which are produced under very short pulse duration are really 'island-like' type multilayered films; and their behavior looks like typical granular (or inhomogeneous alloyed) films - i.e. they show 'bell-like' triangle unsaturated dependence of magnetoresistance.

Upon consideration of our study of granular films and taking into account the complete mutual insolubility of Co and Cu our first idea was to try to get granular Cu-Co films not in a pulse regime, but at constant current density. This was successful.

In previous work on Co-Fe-P and Co-W [15,16] and also other systems where ED films have been produced under constant deposition conditions, it was found that all films were homogeneous. It thus seemed likely that in the Cu-Co system, produced under similar conditions, the same degree of inhomogeneity would be obtained. However, as we shall show, in the case of the Cu-Co system, we also produced samples with a range of inhomogeneities.

The electrolytic composition was: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 30 g/l, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 3.3 g/l, H_3BO_3 6.6 g/l, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 23.3 g/l, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ 10 to 30 g/l [17]. The composition range of the samples investigated was obtained by varying the CoSO_4 concentration in the electrolyte; all other chemical concentrations were held constant. The electrolyte had a pH value of 6.0 and deposition was performed at 20°C with a current density of 5 mA cm^{-2} . The films produced had thickness typically of the order $1 \mu\text{m}$.

Magnetization loops were measured for all samples in the temperature range from 5 to 300 K; all loops had similar characteristics. Some typical results, for a $\text{Co}_{11}\text{Cu}_{89}$ sample are given in Fig.7 The hysteretic behavior at low temperatures, combined with the reversible part of the magnetization curve, which extends over a wide field-range (Fig.7(a)) suggests that we have a mixture of ferromagnetic and superparamagnetic particles. Whereas, at higher temperatures (Fig.7(b)) above the blocking temperature, we observe only superparamagnetism. It is also important to note, in this context, that no sample could be magnetically saturated, even at a temperature of 5 K and the maximum applied field of 5 T.

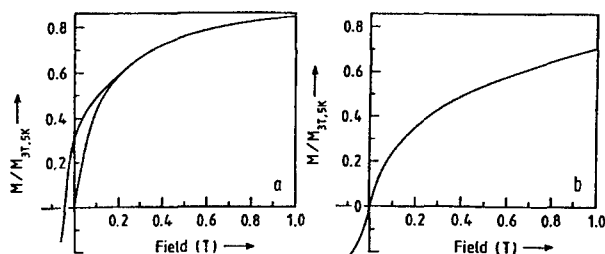


Fig.7. Typical reduced magnetization curves for $\text{Co}_{11}\text{Cu}_{89}$ granular film: a - at 5 K; b - at 300 K

The temperature dependence of the remanence of different granular compositions is shown in Fig.8. We observe curves of continuously varying slope which also differ from sample to sample. This suggests that we have a range of blocking temperatures, depending upon the Co concentration. We have attempted to estimate the maximum blocking temperature for each sample by extrapolating the remanence curves to zero; the maximum blocking temperature increases with increasing Co concentration. The fact that all remanence curves, except that for composition $\text{Co}_{20}\text{Cu}_{80}$, show strong curvatures, suggests a range of blocking temperatures for each sample and a corresponding range of particle sizes present in the films, which we are able to control by varying the deposition conditions.

This also indicates, in our opinion, that we have been successful in producing, immediately after deposition, inhomogeneous alloy systems. The linear variation of the remanence for sample $\text{Co}_{20}\text{Cu}_{80}$ suggests an approximately uniform size of particles in that film.

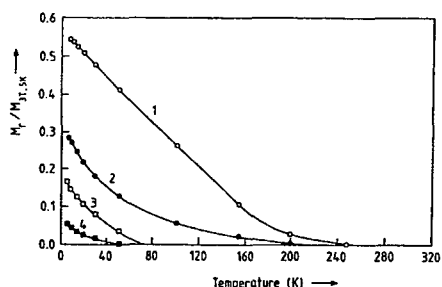


Fig.8. Temperature dependence of the remanence for various samples investigated; values have been normalized with respect to the magnetization at $H = 3\text{T}$ and $T = 5\text{K}$: 1 - $\text{Co}_{20}\text{Cu}_{80}$, 2 - $\text{Co}_{11}\text{Cu}_{89}$, 3 - $\text{Co}_8\text{Cu}_{92}$, 4 - $\text{Co}_6\text{Cu}_{94}$.

In order to estimate the maximum particle size in each sample, we have used the well-known expression: $-K_A v = 25 k_B T_B$, where K_A is the anisotropy energy density, v is the critical particle volume and T_B is the blocking temperature. A value of K_A appropriate for f.c.c. Co has been assumed. The results are summarized in Table 1.

Table 1

Summary of the results obtained for series of CuCo films produced by electrodeposition. The values quoted for the Co concentrations are the averages of chemical and X-ray analyses

Compositions	$T_B(K)$	granular diameter (nm)
Co_6Cu_{94}	55 ± 5	7.6
Co_8Cu_{92}	80 ± 10	8.7
$Co_{11}Cu_{89}$	210 ± 20	12.0
$Co_{20}Cu_{80}$	260 ± 25	12.8

Fig.9 shows the magnetization for an annealed $Co_{0.94}Cu_{0.06}$ film as a function of reduced field and as measured at different temperatures well above the maximum blocking temperature of the sample, 50 ± 5 K. These curves do not superimpose and we conclude that the sample does not exhibit pure superparamagnetism (SPM). Such behavior was typical for the whole range of concentrations investigated, both before and after annealing. In Fig.10 the temperature dependence of the reciprocal of the FC (field cooled) susceptibility is plotted as a function of anneal for sample $Co_{0.94}Cu_{0.06}$. On the assumption that at high temperatures the susceptibility can be represented by a Curie-Weiss law: $\chi \propto (T - T_{int})^{-1}$ where T_{int} is an interaction temperature, T_{int} is obtained by extrapolating the linear part of the curve.

While some caution must be exercised over the interpretation of the results, values obtained for T_{int} are: 20 ± 2 K for the unannealed sample, and 35 ± 4 K and 50 ± 5 K after annealing at 200 and 400°C. On annealing of the sample, there is a gradual increase in curvature of the χ^{-1} plots. Measurements were also made after

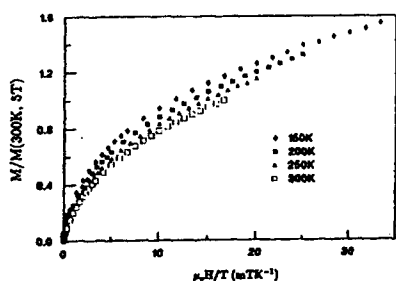


Fig.9. Dependence of magnetization of unannealed Co_6Cu_{94} film as function of reduced magnetic field for the temperature indicated. The magnetization is normalized to its value at $H = 5T$ and $T = 300K$.

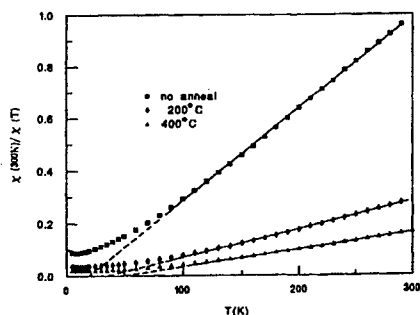


Fig.10. Low-field reciprocal (ZFC-FC method) susceptibility as measured in a field of 5 mT for Co_6Cu_{94} film as a function of anneal at the temperature indicated.

annealing at 600°C, but in this case, we were unable to cool from above the maximum blocking temperature.

So, the temperature interaction is positive and equal $\approx +20$ K for the unannealed $\text{Co}_6\text{Cu}_{94}$ composition, hence, the energy of the cluster interaction is estimated as $E_{\text{int}} = T_{\text{int}} \cdot k_B \approx 1.7 \times 10^{-3}$ eV. This value is comparable with the energy of the magnetic anisotropy of the clusters.

Therefore, at a relatively large positive, i.e. direct ferromagnetic, interaction between the clusters, the second condition of the pure superparamagnetism (Fig.9) does not have to be satisfied. Let us note that $\text{Cu}_{94}\text{Co}_6$ films were fabricated by electrolytic deposition under stationary conditions. During the formation and growth of Cu and Co crystals some clusters can touch each other due to possible anisotropy of their shape (elongation) or formation of a Cu-Co metastable magnetic alloy between certain Co clusters. It is obvious that the interaction between Co clusters in the Cu matrix ought to depend on Co concentration. The size of the magnetic particles depends upon both the electrolytic composition and the detail of the deposition parameters, but typical values, from previous work, are 7 nm for $x = 0.06$, 12 nm for $x = 0.12$ and 15 nm for $x = 0.35$, i.e. they are of the same order of magnitude as the electron mean-free path in transition metals. This is clearly the reason that the spin-dependent component of the electrical conductivity tensor is predominant and this is the basis of the GMR mechanism [18,19].

On annealing of the samples, there is an increase in the GMR (Fig.11), although even after annealing at 600°C, there is no saturation observed in the available field (1.3 T). This is in contrast to the magnetization which, after a corresponding anneal, both increases and saturates in fields of less than 1 T. There is also an increase in the coercivity. This can be understood in terms of a growth of magnetic particle size on annealing. It is well established that the magnitude of the GMR is determined by magnetic cluster sizes, their distribution and also by the sharpness of the composition profile in the vicinity of the particle-matrix boundary; these factors are strongly dependent upon annealing. Work on maximizing GMR by an investigation of these various parameters is in progress and will be reported in due course.

It has been shown that it is possible to produce inhomogeneous alloyed CuCo film by electrodeposition at constant current density from a single solution. Such films have typical superparamagnetic behavior and giant isotropic magnetoresistive properties. It is obvious that the same is also possible for mutually insoluble Cu-Fe system [20]. But it was not unexpected that we would be successful in producing granular alloys from such a completely soluble system as Co-Re [21]. We believe that this is not the limit of the electrodeposition technique and it would be possible to produce homogeneous alloyed films from immiscible metals. We suppose that the above-mentioned Cu-Co system could be obtained not only as a granular system, but also as a homogeneously distributed system. More exactly, we have observed the permanent transition from the multilayered to a granular state in the $\text{Co/Cu} \rightarrow \text{Co-Cu}$ system and the similar transition from granular Co-Cu to homogeneous Co-Cu alloy. It is also possible to vary the sizes of Co clusters in Cu matrix or vice versa - Cu

inclusions in a Co-matrix, by changing the electrochemical regime or preparation conditions.

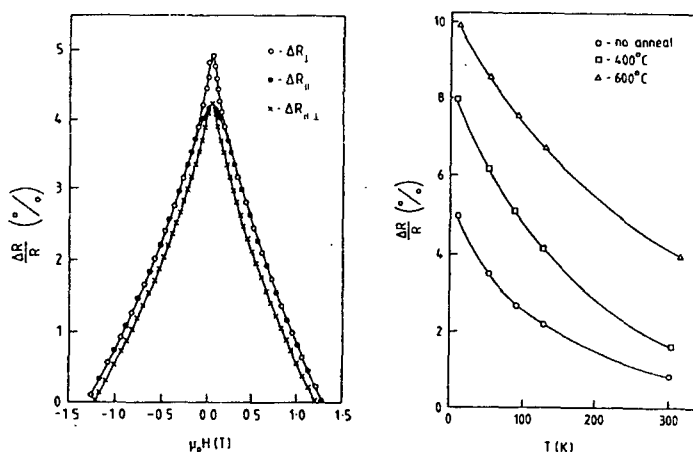


Fig.11. Magnetoresistance of as-deposited $\text{Co}_{20}\text{Cu}_{80}$ film measured at 5K as a function of magnetic field for various orientation indicated (a); and the temperature dependence of the magnetoresistance as a function of annealing for 30 min at a temperature indicated measured with $\mathbf{J} \perp \mathbf{H}$ and both in the film plane.

5. Nanowires

One of the main aims of early studies of nanowires was to achieve a CPP (current perpendicular to plane) giant magnetoresistance, which was expected to be much greater than the conventional CIP (current in plane) effect. Some groups (mainly from Bristol, UK and Jausanu, Switzerland) were successful in this. They produced a wide range of multilayered nanowires. We have demonstrated a further advantage of electrodeposition, namely the possibility of preparing heterogeneous alloys in the form of nanowires having lengths of several mm or tens of mm, and diameters of only a few tens of nm. These nanowires exhibit GMR, the magnitude of which increases on annealing.

Co-Cu heterogeneous alloy nanowires having lengths of several tens of mm and diameters of 20 or 200 nm were deposited in the pores of commercially available anodic aluminum oxide membranes. Unlike the nuclear-track-etched polycarbonate membranes used in previous studies of nanowire, these can be used in annealing studies. Prior to sample growth, all membranes were coated with an evaporated Au layer on the side that was not to be exposed to the electrolyte, in order to produce a conducting substrate for electrodeposition.



Fig.12. Transmission electron micrograph of Co-Cu heterogeneous alloy nanowires electrodeposited in a nuclear track-etched polycarbonate membrane with quoted pore diameter 10 nm and pore density $6 \times 10^8 \text{ cm}^{-2}$.

Although porous aluminum oxide membranes do allow annealing studies, they have the disadvantage that it is relatively difficult to dissolve the aluminum oxide to release the nanowires for structural studies. Some nanowires were therefore electrodeposited in nuclear-track-etched polycarbonate membranes, which can easily be dissolved using chloroform to facilitate characterization by transmission electron microscopy (TEM). Figure 12 shows a TEM image of heterogeneous alloy nanowires electrodeposited at a nominal current density of 3.3 A cm^{-2} , and having a measured room temperature GMR of under 0.5%. It is apparent that the nanowires are highly polycrystalline. No evidence of oxide, reported to be present in some continuous electrodeposited Co-Cu films, was found in these as-deposited nanowires.

Following growth, the room temperature magnetoresistance (MR) of the nanowires was measured with one contact made using Ag DAG to the caps at the tops of the nanowires and the other to the Au layer at the base of the wires. This configuration meant that generally the MR of several nanowires would be measured in parallel. It is immediately apparent that although the absolute magnitude of the MR is small (less than 1%), in both configurations it is negative, showing that we do indeed have GMR, as expected for a heterogeneous Co-Cu alloy. There appears to be symmetric 'shoulders' either side of the central peak in both MR curves, which may be related to details of the magnetization reversal mechanism. This is currently investigated.

This apparent anisotropy in the magnetization reversal process suggests that the nanowire geometry does influence the magnetic properties of the heterogeneous alloy. This could be because some of the Co-rich particles approach the size of the nanowire diameter (20nm); or possibly because even if the nanowire diameter is much larger than the particle dimensions, it may be less than the range over which magnetic interactions are important. Alternatively, during electrodeposition and subsequent annealing, the nanowire geometry could influence the shapes and distributions of the Co-rich magnetic particles, or could lead to stress induced anisotropy in these particles.

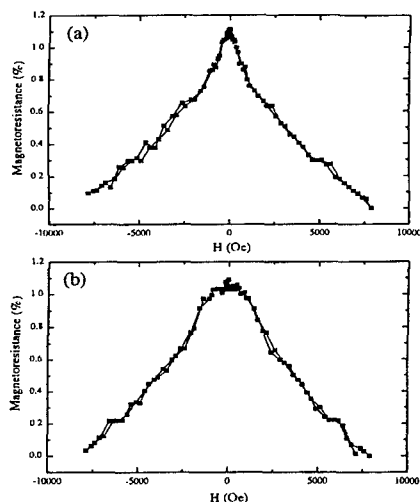


Fig.13. Percentage magnetoresistance for Co-Cu heterogeneous alloy nanowires electrodeposited in an aluminum oxide membrane with quoted pore diameter 200 nm and pore density 10^9 cm^{-2} following by anneal at 400°C for 30 min measured at room temperature with the magnetic field applied (a) parallel and (b) perpendicular to the long axis of

6. Conclusion

A wide range of nanoscaled electrodeposited materials have been discussed. It is clear that all of the above-mentioned types of nanosized structures are constantly being developed in increasing numbers. Research has been undertaken to both obtain additional information about existing materials and to develop new materials with practical application. W. Schwarzacher *et.al.* reported, (still unpublished), a magnetoresistive effect at room temperature of about 70% in multilayered CoNi/Cu nanowires. In previous work by W. Schwarzacher and K. Attenborough, [22], a high sensitivity of about 0.67%/Oe was achieved in electrodeposited $(\text{Co}_x/\text{Cu}/\text{Co}_y/\text{Cu})_n$ multilayers of the 'spin-valve' type. There are several possible ways in which to develop nanoscaled materials with improved properties. For example, work is currently in progress by the authors on multilayered nanowires of spin-valve type [14].

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